# Appendix A

## SSWC Model Application:

## *Calculating critical loads of acidity for acid-impaired New Hampshire lakes using the Steady State Water Chemistry (SSWC) model*

**Calculating critical loads of acidity for acid-impaired New Hampshire lakes using the Steady State Water Chemistry (SSWC) model**

**Abstract**

A critical load model was applied to 65 of New Hampshire's acid impaired ponds.  Critical loads were calculated using the Steady State Water Chemistry (SSWC) model of Henriksen and Posch (2001).

**Background**

New Hampshire listed 76 ponds on the 2004 303(d) list as being impaired for the aquatic life use because of low pH.  To list as impaired, a pond must have at least 10 data points within the past 10 years and at least 3 of the 10 data points must exceed the standard.  For pH, at least three of the 10 pH values needed to be less than 6.5 to be listed as impaired.  Data used to assess ponds for impairment came from several monitoring programs.  The monitoring programs are described below.

> **Remote ponds**:  These are mostly high elevation, remote ponds.  They are sampled, mid-pond at 0.5 meter depth in the spring by helicopter.  Analysis of the complete suite of cations and anions began in 2000.  An average of fours years (2000-2003) of data was used for ponds sampled under this program.

> **Outlet ponds**:  For these ponds the outlets are sampled during spring and fall overturn when outlet water represents average in-lake values.  The complete suite of anions and cations were analyzed beginning in the fall of 1999.  For these lakes, an average of nine data sets was used (fall, 1999 through fall, 2003).

> **Trophic survey lakes**:  Most New Hampshire lakes have been sampled at one time or another under this program.  The complete suite of ions is sampled during the summer at the deep spot in the mid-epilimnion or upper one-third of depth for unstratified lakes.  However, sampling occurs only once every 10 to 20 years in this program so much of the data is dated.  If data was available from one of the above programs, survey data was used only if it occurred during the same time period as the above data.  If data was not available from the above two programs, survey data was used, regardless of age (up to 20 years old).

> **Volunteer Lake Assessment Program:**  Lakes are sampled every year, usually three times per year during the summer period, in this program.  Samples are collected during the summer at the deep spot in the mid-epilimnion or upper one-third of depth for unstratified lakes.  The pH data from this program was used for use impairment assessments, but the program does not collect the anion and cation data needed for the critical loads model.  Recent (last three years) pH and ANC (acid neutralizing capacity) data was used from this program for determining average lake values, but the ion data was from the other programs.

*Data required for calculating critical loads of acidity are:*

> Base cations:  Ca, Mg, Na, K
> Anions:  $SO_4$, $NO_3$, Cl
> Runoff

Some of the available cation and anion data was below the detectable limit and expressed as a "less than" value.  The table below depicts how these "less than' values were used.

| parameter | "less than" value (mg/L) | value used (mg/L) |
|-----------|--------------------------|-------------------|
| Ca | 1 | 0.5 |
| K | 0.4 | 0.2 |
| Na | 1 | 0.5 |
| $NO_3$-N | 0.02 | 0.01 |
| | 0.05 | 0.025 |
| Cl | 2 or 3 | *1 or 0.5 |

* if all chloride values for a particular pond were below detectable (usually the case for the remote ponds), a value of 0.5 mg/L (14 ueq/L) was used (this is based on literature data of chloride values in the northeast remote from road salts); if one or more chloride value was at or above the detectable limit, then a < 2 or < 3 value was listed a 1 mg/L.

Critical loads should be calculated with a yearly average value but are often calculated from a single sample collected in the fall that represents a yearly average (Henriksen and Posch, 2001). Others (Wilander, 2001) have suggested that a minimum value is better than a median value to better protect a lake. In their TMDL submittal, Vermont used spring time values (typically minimum values) for approximately one-half of the lakes and data often collected outside the spring period for the remaining lakes (VTDEC, 2003). For this exercise, average values were used, which, as discussed above, may be spring samples, spring and fall samples, summer samples or a combination of all three seasons.

**Introduction**

The critical loads concept is widely accepted and used in Europe (Henriksen and Posch, 2001) and Canada (Dupont, et al., 2002; Henriksen et al., 2002; Hindar and Henriksen, 1998), but has been criticized by the USEPA (Thornton, 1991) because of its assumptions and lack of predictive capability. However, the dynamic models favored by EPA require much more data and are more complicated and expensive to run. NHDES selected the SSWC model for calculating TMDLs on acid impaired lakes because of its use on similar lakes in eastern Canada, because it is particularly applicable to dilute waters located in granitic bedrock with a thin overburden such as are found in NH and because the State of Vermont used it in 2003 to submit TMDLs for acid impaired Vermont lakes that were approved by USEPA.

The Steady State Water Chemistry model calculates critical loads of acidity based on in-lake water chemistry. A critical load is defined as "a quantitative estimate of the loading of one or more pollutants below which significant harmful effects on specified sensitive elements of the environment are not likely to occur according to present knowledge" (Nilsson and Grennfelt as quoted in Curtis, et al., 2001). Sulfate and nitrate are the major contributors to lake acidification in the northeast and are the pollutants of concern for this TMDL. The model also calculates exceedances of the critical load based on sulfate and nitrate contributions. Exceedances of the critical load are defined as the amount of excess acid above the critical load.

In order to determine a critical load, a critical chemical value for a biological indicator needs to be set. While pH is the measure of acidity (and the reason for impairment listing in New Hampshire), ANC is generally thought to be the better chemical criterion for biological response (Wilander, 2001) and is the endpoint used in the SSWC model. In using the model to calculate TMDLs for ponds violating New Hampshire's pH criterion, the model is used not to necessarily protect biota but to meet a chemical criterion (biological impairment generally doesn't occur until a pH of 6 or less is reached whereas NH's pH criterion is 6.5). The key for using the model is to select an ANC limit that is approximately equivalent to a pH of 6.5. Dupont, et al., (2002) discussed relationships between pH and ANC and quoted Sutton and Small as determining that an ANC of 2 mg/L (40 ueq/L) corresponds to a pH of 6 for Quebec lakes. Vermont used an ANC of 2.5 mg/L (50 ueq/L) as the endpoint for their TMDL calculations .

For this TMDL, an ANC of 3 mg/L (60 ueq/L) was selected as the end point for calculating critical loads for attaining NH's pH criterion of 6.5 (see Figure 1 of this appendix).

**Study area**

See Figure 1 on page 3 in the TMDL report for a map showing the location of the 65 acid impaired ponds.
Table 1 below lists the ponds along with basic physical characteristics.

Table 1.  Physical characteristics of NH's acid impaired ponds

| Lake | Town | Class | Surface area (ha) | Maximum depth (m) | Drainage area (ha) | Elevation (m) |
|---|---|---|---|---|---|---|
| ARMINGTON LAKE | PIERMONT | B | 57.55 | 9.7 | 676.5 | 407 |
| AYERS POND | BARRINGTON | B | 92.11 | 9.1 | 601 | 71 |
| BLACK MOUNTAIN POND | SANDWICH | B | 2.43 | 9.8 | 78.4 | 690 |
| BLACK POND | LINCOLN | B | 2.43 | 13.5 | 33.9 | 503 |
| BOG POND, LITTLE | ODELL | B | 14.97 | 3 | 1238.1 | 622 |
| BOW LAKE | STRAFFORD | B | 469.72 | 21 | 3692.7 | 157 |
| CARTER POND, UPPER | BEANS PURCHASE | B | 0.44 | 4.6 | 7.7 | 1003 |
| CASS POND | RICHMOND | B | 19.59 | 7.9 | 82.8 | 321 |
| CENTER POND | NELSON | B | 14.57 | 10.9 | 193.8 | 430 |
| CHALK POND | NEWBURY | B | 8.5 | 3.6 | 114.1 | 382 |
| COLD POND | ANDOVER | A | 5.99 | 5.5 | 271.1 | 329 |
| COLD SPRING POND | STODDARD | B | 11.78 | 4.8 | 112.3 | 499 |
| COLE POND | ENFIELD | B | 7 | 17.9 | 37.9 | 418 |
| CONNER POND | OSSIPEE | B | 35.01 | 19.2 | 242.8 | 274 |
| CONSTANCE LAKE | PIERMONT | B | 3.64 | 5.5 | 30.9 | 469 |
| CORSER POND | ERROL | B | 2.02 | 4.9 | 59.3 | 610 |
| DARRAH POND | LITCHFIELD | B | 7 | 8.4 | 35.9 | 54 |
| DERBY POND | CANAAN | B | 4.05 | 3.6 | 47.3 | 617 |
| DUBLIN POND | DUBLIN | B | 96.6 | 31.1 | 279.4 | 451 |
| DUTCHMAN POND | SPRINGFIELD | B | 11.29 | 3 | 47.6 | 470 |
| EAST POND | LIVERMORE | B | 2.7 | 7.9 | 113.7 | 774 |
| ECHO LAKE | FRANCONIA | B | 11.49 | 11.6 | 124.1 | 589 |
| FLAT MOUNTAIN POND (1&2) | WATERVILLE | B | 15.66 | 5.5 | 574.5 | 704 |
| FROST POND | JAFFREY | B | 41.8 | 3.7 | 116.2 | 334 |
| GILMORE POND | JAFFREY | B | 46.54 | 13.1 | 99.2 | 321 |
| GRANITE LAKE | STODDARD | B | 92.19 | 28.9 | 1084 | 390 |
| GREELEY POND (UPPER) | LIVERMORE | B | 0.81 | 7.9 | 63 | 684 |
| GREGG LAKE | ANTRIM | B | 78.95 | 11 | 1123.8 | 321 |
| HALFMILE POND | ENFIELD | B | 2.75 | 4.7 | 33.1 | 552 |
| HALL POND, MIDDLE | SANDWICH | B | 3.24 | 17 | 229.2 | 445 |
| HARRISVILLE POND | HARRISVILLE | B | 48.56 | 12.5 | 2710.6 | 402 |
| ISLAND POND | WASHINGTON | B | 81.83 | 16.8 | 647.5 | 429 |
| IVANHOE, LAKE | WAKEFIELD | B | 27.52 | 6.1 | 153.2 | 182 |
| JENNESS POND | NORTHWOOD | B | 94.09 | 8.5 | 640.1 | 200 |
| KNOWLES POND | NORTHFIELD | A | 24.28 | 17 | 84.8 | 227 |
| LAUREL LAKE | FITZWILLIAM | B | 62.73 | 13.4 | 269.1 | 335 |
| LEDGE POND | SUNAPEE | A | 44.56 | 5.2 | 256 | 399 |
| LONESOME LAKE | LINCOLN | B | 11.01 | 2.6 | 142.6 | 838 |
| LONG POND | LEMPSTER | B | 48.56 | 20.3 | 374.2 | 472 |
| LONG POND | NORTHWOOD | B | 40.55 | 14.7 | 386.3 | 176 |

| Lake | Town | Class | Surface area (ha) | Maximum depth (m) | Drainage area (ha) | Elevation (m) |
|---|---|---|---|---|---|---|
| LOON LAKE | PLYMOUTH | B | 45.28 | 8.8 | 973.7 | 149 |
| MAY POND | WASHINGTON | B | 60.3 | 7.6 | 1811.8 | 489 |
| MILLEN POND | WASHINGTON | B | 63.13 | 12.6 | 324.2 | 482 |
| MONOMONAC, LAKE | RINDGE | B | 287.78 | 7.8 | 4827.1 | 318 |
| NORTHWOOD LAKE | NORTHWOOD | B | 277.99 | 6.3 | 6064.7 | 157 |
| NUBANUSIT LAKE | NELSON | B | 289.35 | 30.2 | 1569 | 419 |
| PEAKED HILL POND | THORNTON | B | 4.45 | 4.8 | 108.2 | 352 |
| PECKER POND | RINDGE | B | 9.71 | 4.5 | 79.1 | 369 |
| PLEASANT LAKE | DEERFIELD | B | 199.71 | 19.8 | 925.1 | 176 |
| PRATT POND | NEW IPSWICH | B | 15.58 | 2.7 | 172.1 | 376 |
| ROCKWOOD POND | FITZWILLIAM | B | 30.76 | 6.7 | 367.1 | 339 |
| RUSSELL POND | WOODSTOCK | B | 15.78 | 22.5 | 149.6 | 502 |
| SAND POND | MARLOW | B | 64.38 | 18.3 | 315.9 | 470 |
| SAWYER POND, LITTLE | LIVERMORE | B | 4.45 | 8.8 | 24.6 | 631 |
| SILVER LAKE | HARRISVILLE | B | 134.64 | 26.2 | 607.4 | 402 |
| SKATUTAKEE, LAKE | HARRISVILLE | B | 105.58 | 6.2 | 3826.8 | 366 |
| SOLITUDE, LAKE | NEWBURY | B | 2.02 | 6.7 | 10.5 | 722 |
| SPECTACLE POND | GROTON | B | 18.53 | 11.8 | 84.5 | 250 |
| STINSON LAKE | RUMNEY | B | 141.64 | 23.5 | 2084.3 | 397 |
| STONE POND | MARLBOROUGH | B | 26.26 | 14.6 | 191 | 395 |
| SUNCOOK POND, LOWER | BARNSTEAD | B | 99.27 | 4.9 | 14152.4 | 168 |
| SWEAT POND | ERROL | B | 2.43 | 7 | 65.2 | 594 |
| THORNDIKE POND | JAFFREY | B | 107.24 | 7 | 1002 | 353 |
| WACHIPAUKA POND | WARREN | B | 9.02 | 9.1 | 79.8 | 455 |
| WHITE LAKE | TAMWORTH | A | 49.78 | 14.6 | 362 | 134 |

**Methods**

**Calculating critical loads**
The SSWC model is based on the principle that excess base cation production within a catchment area should be equal to or greater than the acid anion input, thereby maintaining the ANC above a pre-selected level (Reynolds and Norris, 2001). The model assumes steady state conditions, assumes that all sulfate in runoff originates from anthropogenic deposition and sea salt spray and is not adsorbed or retained in the watershed, and assumes that all chloride in the water comes from sea salt spray. Given a pre-selected critical ANC value, the critical load of acidity is simply the input flux of acid anions from atmospheric deposition, which gives the critical ANC when subtracted from the pre-industrial flux of base cations. Concentrations are multiplied by runoff Q to convert to fluxes. For a more detailed discussion of the SSWC model, see papers by Curtis, et al., 2001; Henriksen and Posch, 2001; and Henriksen, et al., 2002.

The critical load of acidity is expressed as:

$$CL_{ac} = ([BC^*]_o - [ANC]_{limit}) * Q$$

where:

$CL_{ac}$ = critical load of acidity (S+N)
$[BC^*]_o$ = pre-industrial concentration of base cations (corrected for sea salt)
$[ANC]_{limit}$ = critical ANC concentration;

$$Q \qquad = \text{annual runoff (m/yr)}$$

The SSWC model uses in-lake water chemistry for the following inputs:

$BC$    = sum of base cations (Ca, Mg, Na, K)
$SO_4$   = in-lake sulfate concentration
$NO_3$   = in-lake nitrate concentration

*Sea salt corrections*
The model applies a sea salt correction to the water chemistry concentrations. The equations below were applied to the Vermont lakes for their acid TMDL, and was applied to all the New England states and eastern Canadian provinces for the NEG/ECP assessment (Dupont et al, 2002). The equations correct for sea salt and convert concentrations from mg/L to ueq/L for use in the model. An asterisk ($^*$) indicates the value has been corrected for sea salt (in the equations, $*$ means multiplied by) and "U" before an ion indicates that it has been converted to ueq/L.

$UCa^*$      $= (Ca - (Cl * 0.0213)) * 49.9$
$UMg^*$     $= (mg - (Cl * 0.0669)) * 82.26$
$UNa^*$      $= (Na - (Cl * 0.557)) * 43.5$
$UK^*$        $= (K - (Cl * 0.0206)) * 25.57$
$USO_4^*$    $= (SO_4 - (Cl * 0.14) * 20.82$
$UNO_3^*$    $= (NO_3\text{-N}) * 71.4$
$UCl$        $= Cl * 28.21$

note: $NO_3$-N $* 71.4$ converts nitrate nitrogen in mg/L to the nitrate ion in ueq/L

*Pre-industrial base cation concentration and F factor*
The pre-industrial (pre-acidification) non-marine flux of base cations from the watershed to a lake needs to be estimated. It cannot be estimated simply by measuring present day runoff concentrations because post-industrial acidic deposition has increased the leaching of base cations through ion exchange in the soils. Empirical relationships are invoked and an F factor is employed, which is defined as a ratio of the change in non-marine base cation concentrations due to changes in strong anion concentrations (Brackke, et al., 1990). The original F factor equation was recently modified to account for catchment areas with high and low runoff (Hindar and Henriksen, 1998). A more detailed discussion of the procedure can be found in Curtis et al., (2001) and Henricksen and Posch (2001). Suffice it to say here that New Hampshire used the same assumptions and equations as used by Vermont for their acid pond TMDL report (Pembrook, 2003).

The equation below presents the procedure for calculating the pre-industrial non-marine flux of base cations, where the subscripts $_o$ and $_t$ refer to original (pre-industrial) and current respectively, and the superscript $^*$ refers to corrected for sea-salt.

$$BC^*_o \qquad = BC^*_t - F \text{ factor } (USO4^*_t - USO4^*_o)$$

Where:
$BC^*_t$        = sum of present day non-marine base cations    $(UCa^* + UMg^* + UNa^* + UK+)$

F-factor    = annual base cation flux accounting for runoff in the catchment, which is $= \sin\{[(\pi/2)*Q*BC_t]/S\}$. $S$ = base cation flux at which $F = 1$. $S = 400$ meq/m$^2$/yr was considered appropriate for Ontario lakes, was used by Vermont for their acid pond TMDL and is used here. $Q$ = runoff.

$USO_4^*{}_t$     = current non-marine, in-lake sulfate concentration

$USO_4^*{}_o$    = pre-acidification sulfate concentration. Vermont used estimates for Ontario (Henricksen, et al., 2002) that were also used for northeast North America (Jacques, et al., 2002) and are used here.

*ANC Limit*

The $[ANC]_{limit}$ is the lowest ANC concentration that does not damage selected biota (Henriksen and Posch, 2001). The model allows for an $[ANC]_{limit}$ to be pre-selected depending on the geographic area. Vermont chose an $[ANC]_{limit}$ of 2.5 mg/L (50 ueq/L). This is in line with limits of 40 to 50 ueq/L chosen in other North American studies (Hindar and Henricksen, 1998; Dupont, et al., 2002). For New Hampshire, the SWCC model is being used to estimate load reductions necessary to allow the ponds to meet the water quality criterion (pH = 6.5 or greater), which will require greater reductions than needed to protect biota. A pH of 6.0 is generally thought to be the criterion to protect most aquatic organisms (see, e.g., Schindler, 1988) and this is approximately equivalent to an ANC of 40 ueq/L for Quebec lake waters (Small and Sutton, 1986). Based on data from the ponds being evaluated, NHDES determined that an ANC of 3.0 mg/L (60 ueq/L) approximates a pH of 6.5 (see Figure 1 below) and have therefore selected 3.0 mg/L as the $[ANC]_{limit}$.

Figure 1. pH vs ANC for acid impaired ponds
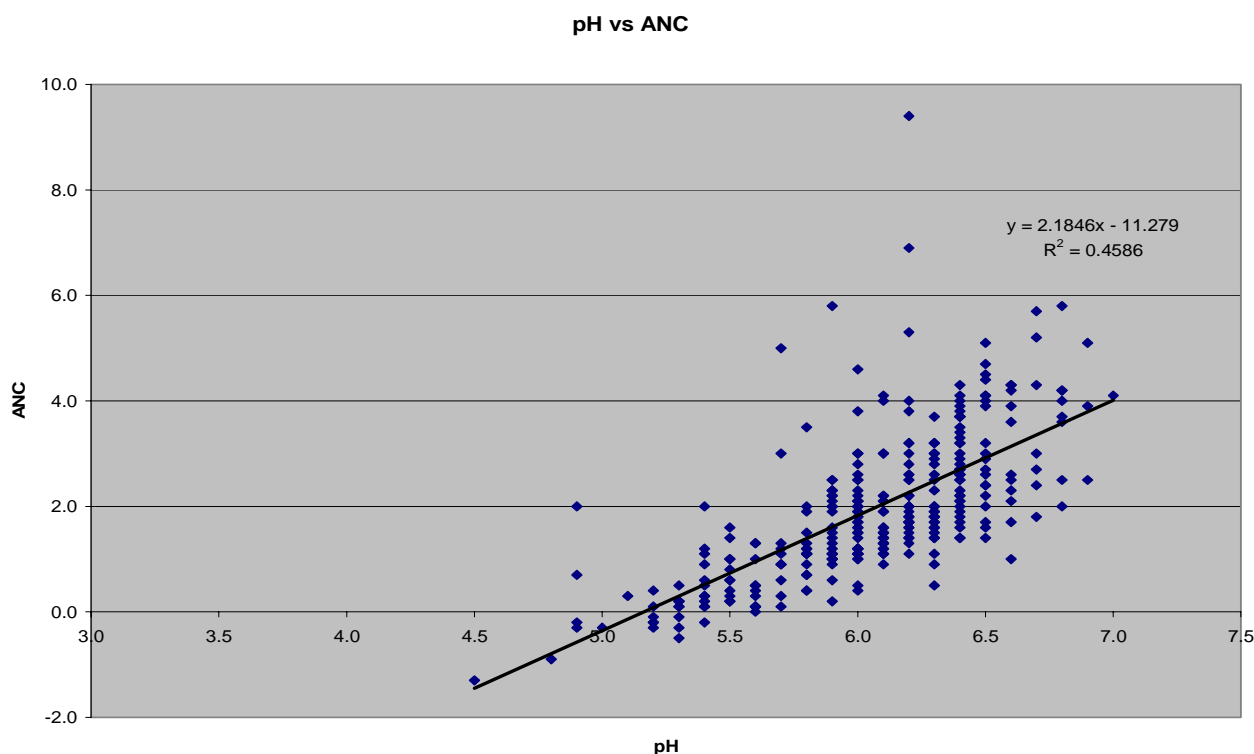


*Annual surface runoff estimates*: Q

Annual estimates of surface runoff (Q) were obtained from Knox and Nordenson (1955) or Randall (1996).

**Interpreting critical load values**

The calculated critical load for a lake is considered to be an inherent property of the lake and its catchment area. A positive value indicates that the waterbody has some tolerance for acid inputs. The greater the value, the greater the tolerance for acidification. Very high values suggest conditions may be acceptable for sensitive organisms regardless of deposition scenarios whereas low values suggest sensitivity to acidification (Hindar and Henriksen, 1998).

Negative critical load values occur when the selected $ANC_{limit}$ is higher than the calculated original base cation concentration ($BC_o^*$). Such results imply that the water quality criterion (pH 6.5 as represented by ANC 3.0) is greater than what nature provides. In other words, the natural conditions were such that the original (pre-industrialization) ANC was lower than the selected ANC for protection of biota (Henriksen, et al., 1992). The critical load for such lakes is converted to zero in order to calculate exceedances. For these lakes with a critical load of zero, the critical load will always be exceeded even assuming the strongest emission reduction scenarios, and the lakes will never attain a pH of 6.5.

The critical loads for New Hampshire's acid impaired ponds ranged from -147 (Island Pond in Washington) to 149 (Upper Greeley Pond) with a mean value of 44 (the negative values were averaged as negative values). Despite the wide range in values, caused primarily by just two or three ponds, the mean value of all lakes was of the same order of magnitude as the mean value that Vermont determined for their acid impaired ponds (29).

**Sensitivity of the model**

The SSWC model is highly sensitive to two parameters: the $ANC_{limit}$ and the F-factor. The $ANC_{limit}$ selected was based on the pH water quality criterion of 6.5 and the relationship between pH and ANC. DES chose a limit of 60 ueq/L (3.0 mg/L), which is more protective than the 50 ueq/L limit used by Vermont (VTDEC, 2003) and the 40 ueq/L limit used by for the NEG/ECP analysis (Dupont, et al., 2002). Lowering the $ANC_{limit}$ would increase the critical load values and decrease the excess load values.

The F-factor accounts for the rate of base cation leaching from the watershed. Vermont, the NEG/ECP analysis for northeast North America and studies of lakes in Ontartio, Canada (Henriksen et al., 2002; Hindar and Henriksen, 1998) all used an F-factor based on a Norwegian estimate that takes into account high and low runoff from a catchment area. The same F-factor was assumed appropriate for New Hampshire lakes.

**Acknowledgement**

**Literature Cited**

Brakke, D.F., A. Henriksen and S.A. Norton. 1990. A variable F-factor to explain changes in base cation concentrations as a function of strong acid deposition. Verh. Internat. Verein. Limnol. *24*:146-149.

Curtis, C.J., B. Reynolds, T.E.H. Allott and R. Harriman. 2001. The link between the exceedance of acidity critical loads for freshwaters, current chemical status and biological damage: a re-interpretation. Water, Air, and Soil Pollution: *Focus 1*: 399-413.

Dupont, J., T.A. Clair, C. Gagnon, D.S. Jeffries, S. Kahl, S. Nelson and J. Peckenham. 2002. Estimation of critical loads of acidity for lakes in New England and Eastern Canada. Unpublished manuscript prepared for the New England Governors and Eastern Canadian Premiers' Acid Rain Steering Committee.

Henriksen, A., P.J. Dillon and J. Aherne. 2002. Critical loads of acidity for surface waters in south central Ontario, Canada: regional application of the steady-state water chemistry (SSWC) model. Can J. Fish. Aquat. Sci. *59*: 1287-1295.

Henriksen, A., J. Kamari, M. Posch and A. Wilander. 1992. Critical loads of acidity: Nordic surface waters. Ambio *21(5)*: 356-363.

Henriksen, A. and M. Posch. 2001. Steady-state models for calculating critical loads of acidity for surface waters. Water, Air, and Soil Pollution: *Focus 1*: 375-398.

Hindar A. and A. Henriksen. 1998. Mapping of critical loads and critical load exceedances in the Killarney Provincial Park, Ontario, Canada. Norwegian Institute for Water Research, Report No. O-97156. 36pp.

Knox, C.E. and T.J. Nordenson. 1955. Average annual runoff and precipitation in the New England-New York area. Hydrologic Investigations Atlas HA-7. U.S. Geological Survey. Washington, D.C.

Pembrook, H. 2003. Calculating critical loads of acidity and exceedances for acid-impaired lakes in Vermont using the Steady State Water Chemistry (SSWC) model. App. A of Vermont Department of Environmental Conservation TMDL for 30 acid impaired lakes. 17pp.

Randall, A.D. 1996. Mean annual runoff, precipitation and evapotranspiration in the glaciated northeastern United States, 1951-80. Open-file Report 96-395. Plate 1 & 2. United States Geological Survey.

Reynolds, B. and D.A. Norris. 2001. Freshwater critical loads in Wales. Water, Air, and Soil Pollution: *Focus 1*: 495-505.

Schindler, D.W. 1988. Effects of acid rain on freshwater ecosystems. Science *239*: 149-157.

Thornton, K.W. 1991. Methods for projecting future changes in surface water acid-base chemistry. Rpt. No. 14. pp 125-128. In: Irving, P.M. [ed]. 1991. Acidic Deposition: State of Science and Technology. USEPA. Washington. 265pp.

Vermont Department of Environmental Conservation. 2003. Total maximum daily load: 30 acid impaired lakes.

Wilander, A. 2001. How are results from critical load calculations reflected in lake water chemistry? Water, Air, and Soil Pollution: *Focus 1*: 525-532.